



SUBSTITUTE SPECIFICATION

SELECTRIVE REDUCTION TYPE, HIGH TEMPERATURE SUPERCONDUCTOR  
AND METHODS OF MAKING THE SAME

5

Technical Field

This invention relates to a selective reduction type, high temperature superconductor, which is a copper (Cu) oxide, high temperature superconductor that permits doping with  
10 positive holes by selectively reducing constituent elements (atoms). This superconductor can be used in large scale superconducting power transmission, superconducting power storage or reserve, superconducting electronics such as a high performance Josephson device, a high frequency device or the  
15 like. The invention also relates to methods of making such a superconductor.

Background Art

Conventional Cu-oxide family, high temperature super-  
20 conductors have been prepared doping with positive holes, by oxidation, to raise the contents of the superconducting carriers. Such a high temperature superconductor, however, may cause the carriers to reduce in concentration due to diffusion or bleeding of oxygen atoms by increased temperature.  
25 This leads to a depletion in superconductivity of the superconductor.

Also, doping with positive holes to obtain a higher carrier concentration has been thought to require a higher oxygen partial pressure, and it has so far been unattainable  
30 to prepare a superconductor of the type described by doping with positive holes to raise the carrier concentration in a reduction process conditioned under low partial pressure or vacuum. Since it has been found impossible to increase the concentration of positive holes by reduction, i.e., by  
35 lowering the oxygen partial pressure, the conventional high temperature superconductors have the problem that they

have a limited carrier concentration and are thus low and unsatisfactory in their superconducting properties that include the critical temperature  $T_c$ , critical current density  $J_c$ , irreversible magnetic field  $H_{irr}$ . It has therefore been  
40 sought to solve the problem of bringing into realization a high temperature superconductor of a reduced oxygen concentration.

With these problems taken into account, it is  
45 accordingly a first object of the present invention to provide a selective reduction type, high temperature superconductor that permits doping with positive holes by selectively reducing constituent elements (atoms).

Another object of the present invention is to provide  
50 a method of making a selective reduction type, high temperature superconductor.

#### Disclosure of the Invention

In order to achieve the first object mentioned above,  
55 there is provided in accordance with the present invention, a selective reduction, high temperature superconductor, wherein it has a portion of its constituent elements selectively reduced whereby it has a superconducting layer thereof doped with positive holes.

60 The present invention also provides a selective reduction type, high temperature superconductor that has a portion of its constituent elements selectively reduced whereby there are formed in superconducting layers a first and a second region doped overly and doped optimally with  
65 superconducting carriers, respectively.

The present invention further provides a selective reduction type, high temperature superconductor that has a portion of its constituent elements selectively reduced whereby the superconductor as a whole has a superconducting  
70 carrier concentration such that it is held doped overly or doped optimally with superconducting carriers.

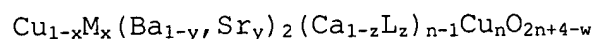
The present invention also provides a selective reduction

type, high temperature superconductor that has on each of an upper and a lower surface of a unit lattice thereof a charge supply layer  
75 having each of a portion of Cu atoms substituted with a selectively reducible atom.

The present invention also provides a selective reduction type, high temperature superconductor in which the said superconducting layers have an upper and a lower surface  
80 constituted by a  $\text{CuO}_2$  layer of 5-coordination and a layer other than the upper and lower constituted by a  $\text{CuO}_2$  layer of 4-coordination, the said  $\text{CuO}_2$  layer of 5-coordination and 4-coordination having been over- and optimum-doped, respectively, by selective reduction.

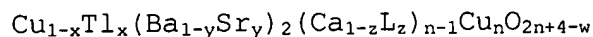
85 Further, the present invention provides a selective reduction type, high temperature superconductor having a selectively over-doped and/or a selectively optimum-doped construction.

The present invention further provides a selective  
90 reduction type, high temperature superconductor, characterized in that it is made of a (Cu, M) group, high temperature superconducting material, which can be described by composition formula:



95 where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  
100  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

The present invention also provides selective reduction type, high temperature superconductor, characterized in that it is made of a (Cu, Tl) group, high temperature superconducting material that can be described  
105 by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x$

$\leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

110 The present invention also provides a selective reduction type, high temperature superconductor, characterized in that it is made of a (Cu, Tl) group, high temperature superconducting material that can be described by composition formula:

115 
$$\text{Cu}_{1-x}\text{Tl}_x(\text{Ba}_{1-y}\text{Sr}_y)_2(\text{Ca}_{1-z}\text{L}_z)_2\text{Cu}_3\text{O}_{10-w}$$

where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

120 The present invention also provides a selective reduction type, high temperature superconductor, characterized in that it is made of a high temperature superconducting material that can be described by composition formula:

$$\text{Cu}_{1-x}\text{Tl}_x(\text{Ba}_{1-y}\text{Sr}_y)_2(\text{Ca}_{1-z}\text{L}_z)_3\text{Cu}_4\text{O}_{12-w}$$

125 where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

130 The present invention further provides a selective reduction type, high temperature superconductor, characterized in that selective over- or optimum-doping is effected by decrease in the valence number of ions of a constituent element by decrease in the oxygen concentration, that is by selective reduction, or by varying (increasing or decreasing) oxygen concentration.

135 The present invention also provides a selective reduction type, high temperature superconductor, characterized in that it is a selectively over-doped type or a selectively optimum-doped type, high temperature superconductor in which n is any one of 3, 4, 5, 6 and 7.

140 The present invention further provides a selective reduction type, high temperature superconductor having a construction that the reduction of selectively reducible ions causes the ions in the charge supply layers to receive electrons in their outer shell orbits, thereby providing holes

145 in the  $\text{CuO}_2$  layer of 5-coordination of a said superconducting layer.

The present invention further provides a selective reduction type, high temperature superconductor having a construction that it has a superconducting anisotropy of not  
150 greater than 10 and a coherence distance of not less than 3 angstroms.

The present invention further provides a selective reduction type, high temperature superconductor having a construction that said selective reduction transforms its  
155 natural superconducting wave function that is of a d-wave high in spatial anisotropy to a wave function of a  $(d + is)$  wave that has also a property of an s-wave lacking of spatial anisotropy.

A selective reduction type, high temperature  
160 superconductor so constructed as mentioned above according to the present invention can be prepared in a reducing atmosphere or can in use have its oxygen content decreased, yet still maintain a high critical temperature  $T_c$ , while providing a reduced aniso-superconductivity  $\gamma$ , a high  
165 critical current density  $J_c$  and a high critical magnetic field  $H_{irr}$ .

Stated otherwise, a selective reduction type, high temperature superconductor according to the present invention is provided with a crystalline and an electronic structure  
170 that permits achieving improved  $J_c$  and  $H_{irr}$  while maintaining  $T_c$  high. Moreover, provided with a superconducting wave function of a  $(d + is)$  wave, it is low in superconducting anisotropy. With these advantages, it can be used as a high performance, high temperature superconductor in a variety of  
175 industrial sub-fields concerned.

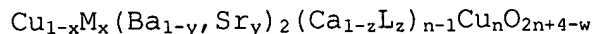
In order to achieve the second object mentioned above, the present invention provides a method of making a selective reduction type, high temperature superconductor, which comprises the steps of: preparing a high temperature  
180 superconductor, and heat-treating the prepared high

temperature superconductor in a reducing atmosphere.

The present invention also provides a method of making a selective reduction type, high temperature superconductor, comprising the steps of: using an amorphous film as a precursor  
185 of high temperature superconductor; causing the amorphous film to grow epitaxially by amorphous phase epitaxy; and heat-treating in a low oxygen, reducing atmosphere the amorphous film that has grown epitaxially.

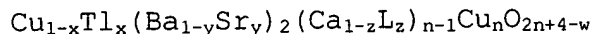
The present invention further provides a method of  
190 making a selective reduction type, high temperature superconductor, comprising the steps of: causing added constituent elements to develop their self-assembling (or self-forming) effect; and causing the high temperature superconductor to grow epitaxially by the self-assembling  
195 effect.

A method of making a selective reduction type, high temperature superconductor of the present invention as mentioned above is applicable to making a (Cu, M) group, selective reduction type, high temperature superconductor expressed by composition  
200 formula:



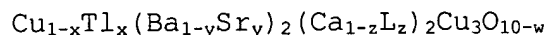
where M represents ions of one or more polyvalent metallic elements selected from the class which consists of Tl, Bi, Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re  
205 and Os; L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  
 $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

A method of making a selective reduction type, high temperature superconductor of the present invention as mentioned  
210 above is also applicable to making a (Cu, Tl) group, selective reduction type, high temperature superconductor expressed by composition formula:



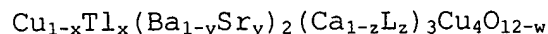
where L represents one or more elements selected from the class  
215 which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  
 $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

A method of making a selective reduction type, high temperature superconductor of the present invention as mentioned above is also applicable to making a (Cu, Tl) group, selective reduction type, high temperature superconductor expressed by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

A method of making a selective reduction type, high temperature superconductor of the present invention as mentioned above is also applicable to making a selective reduction type, high temperature superconductor expressed by composition formula:



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

A method of making a selective reduction type, high temperature superconductor of the present invention so constructed as mentioned above permits manufacturing a positive hole dopable or doped selective reduction type, high temperature superconductor.

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#### Brief Description of the Drawings

The present invention will better be understood from the following detailed description and the drawings attached hereto showing certain illustrative forms of embodiment of the present invention. In this connection, it should be noted that the embodiments illustrated in the accompanying drawings hereof are intended in no way to limit the present invention but to facilitate an explanation and understanding thereof.

In the drawings:

250 Fig. 1 is a diagram showing modeled crystalline structures of a selective reduction type, high temperature superconductor according to the present invention in which

A and B show unit lattices with  $n = 1$  and  $n = 2$ , respectively;

255 Fig. 2 is a diagram showing modeled crystalline structures of a selective reduction type, high temperature superconductor according to the present invention in which A, B and C show unit lattices with  $n = 3$ ,  $n = 4$  and  $n = 5$ , respectively;

260 Fig. 3 is a diagram showing the temperature dependency of the electrical resistivity according to a first form of embodiment of the present invention annealed at various temperatures in a nitrogen atmosphere;

Fig. 4 is a diagram showing thermo-analysis data according to the first form of embodiment of the invention;

265 Fig. 5 is a diagram showing change of the hole concentration with temperature according to the first form of embodiment of the invention annealed in nitrogen atmosphere;

270 Fig. 6 is a diagram showing relationships between  $T_c$ , normal conduction electrical resistivity, carrier concentration, weight's rate of change of, and annealing temperature for, specimens according to the first form of the invention annealed in nitrogen atmosphere;

275 Fig. 7 is a diagram showing an electronic state according to the first form of embodiment of the invention that is high in oxygen concentration;

Fig. 8 is a diagram showing an electronic state according to the first form of embodiment of the invention that is low in oxygen concentration; and

280 Fig. 9 is a diagram showing an X-ray diffraction analysis pattern according to a second form of embodiment of the present invention.

#### Best Modes for Carrying Out the Invention

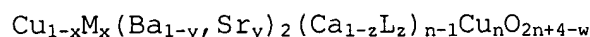
285 Hereinafter, the present invention for a selective reduction type, high temperature superconductor and a method of its making will be described in detail with respect to suitable forms of embodiment thereof illustrated in Figs. 1



to 9.

290 While the conventional methods for increasing the  
carrier concentration in a high temperature superconductor  
rely either on oxidation by heat treatment in high pressure  
oxygen or on substitution to form elements of varying valence  
numbers, a selective reduction type, high temperature  
295 superconductor according to the present invention is  
characterized in that it has an increased concentration of  
positive holes achieved by reduction, namely by lowering the  
oxygen concentration, which permits enhancing its  $T_c$  (critical  
temperature),  $J_c$  (critical current density) and  $H_{irr}$  (critical  
300 magnetic field) to a considerable extent.

A Cu-oxide super conductor of the present invention:



includes charge supply layers formed by  $\text{Cu}_{1-x}\text{M}_x$  plane that make  
up the upper and lower surfaces of a unit lattice, and super-  
conducting layers that make up the other layers (other than  
305 the upper and lower) of the unit lattice, namely those formed  
by  $\text{CuO}_2$  planes of a pyramidal  $\text{CuO}_5$  cluster, i.e.,  $\text{CuO}_2$  planes  
of 5 coordination number and those formed by  $\text{CuO}_2$  planes of  
a planar  $\text{CuO}_4$  cluster, i.e.,  $\text{CuO}_2$  planes of 4 coordination  
310 number, these different superconducting layers being laid  
alternately one on another.

Figs. 1 and 2 illustrate modeled crystal structures of  
selective reduction type, high temperature superconductors  
of the present invention. These modeled crystal structures  
315 are illustrated for a  $\text{CuBaCa}_{n-1}\text{O}_{2n+4-w}$  where  $1 \leq n \leq 16$  and  $0 \leq w \leq 4$ ,  
in particular with respect to examples thereof in which  
 $n$  is an integer from 1 to 5.

Fig. 1A is for a unit lattice where  $n$  is 1, and Fig.  
1B is for a unit lattice where  $n$  is 2. In Fig. 2, A, B and  
320 C are for unit lattices where  $n$  is 3, 4 and 5, respectively.

Referring to Fig. 2A, a selective reduction type, high  
temperature superconductor of the present invention comprises  
a pair of  $\text{Cu}_{1-x}\text{M}_x$  planes 1, 1 that constitute its charge supply  
layers, a  $\text{CuO}_2$  plane 2 of 5 coordination number that constitutes

325 a superconducting layer and a  $\text{CuO}_2$  plane 3 of 4 coordination number that constitutes a superconducting layer.

According to a selective reduction method of the present invention, a superconducting layer is formed as a  $\text{CuO}_2$  plane 2 of coordination number 5 in which the density of  
330 positive holes is such that it is either overly (excessively) or optimally doped with them, or nearly so doped, and is formed as a  $\text{CuO}_2$  plane 3 of coordination number 4 in which the density of positive holes is such that it is optimally or nearly optimally doped with them. To wit, the method permits forming  
335 an excessively or optimally doped  $\text{CuO}_2$  plane and an optimally doped  $\text{CuO}_2$  plane selectively and separately.

A selective reduction method of the present invention is a method whereby polyvalent, reducible ions (e.g., Tl ion) substituted for a portion of Cu ions in the charge supply layers  
340 of a high temperature superconductor are reduced (their ionic valence is reduced) by decreasing the oxygen content in the high temperature superconductor (e.g., by heat treatment in a reducing atmosphere). It is by this reduction of reducible substituted ions that the electronic and band structures of  
345 a Cu-oxide high temperature superconductor vary and a mechanism is revealed that permits doping with positive holes. It should also be noted at this point that term "selective reduction type high temperature superconductor" as used herein, of the present invention is intended to refer to a high  
350 temperature superconductor that comprises a pair of charge supply layers constituted by an upper and a lower surface of a unit superconductor lattice having each of a portion of Cu atoms I these surfaces substituted with polyvalent, reducible ions and having these substitutional ions exclusively and  
355 selectively reduced, and a superconducting layer as a layer other than those upper and lower surfaces.

Fig. 7 is a diagram that shows an electronic state of the  $\text{CuO}_2$  plane 2 of an afore-mentioned Cu-oxide, high temperature superconductor in case its oxygen content is high,  
360 and Fig. 8 is a diagram that shows an electronic state of the

CuO<sub>2</sub> plane 2 of an afore-mentioned Cu-oxide, high temperature superconductor in case its oxygen content is decreased.

Referring to Figs. 7 and 8, if the oxygen content is high it is seen that Tl ions present in a charge supply layer  
365 is in a plus (+) trivalent state and the Tl6s level is above the Fermi level. If as a result of oxygen reduction the oxygen content is lowered, Tl ions take a plus monovalent state and the Tl6s level lies below the Fermi level.

As a consequence, electrons are pulled out of the CuO<sub>2</sub>  
370 plane of coordination number 5 as a superconducting layer and holes are supplied into the CuO<sub>2</sub> plane of coordinate number 5, the superconducting layer. In this way, reducing reducible polyvalent ions such as Tl ions by decreasing the oxygen content, namely supplying positive holes by selective  
375 reduction permits increasing the carrier concentration. In the context hereof, supplying positive holes by selective reduction is referred to as selective doping.

Using selective doping enables producing a high performance, high temperature superconductor. For example,  
380 heat-treating in a reducing atmosphere such a high temperature superconductor formed in an overly doping composition to decrease oxygen by a certain amount decreases the carrier concentration because of the superconducting layers losing oxygen, but permits the CuO<sub>2</sub> plane 2 of coordination number  
385 5 as one superconducting layer to stay in an overly doped state by being injected with holes by selective doping.

On the other hand, the 4-coordination CuO<sub>2</sub> plane 3 providing for the other superconducting layer is not doped with holes and therefore has a reduced carrier concentration,  
390 staying in an optimally doped state. Thus, a makeup is provided in which while the superconducting layers as a whole are overly doped, there also exists an optimally doped CuO<sub>2</sub> plane. The method mentioned above is referred to herein as selective over-doping method. Likewise, it is also possible to make both  
395 the 5-coordination and 4-coordination CuO<sub>2</sub> plane superconducting layers doped optimally as a whole in their

carrier concentration. This alternative method is referred to herein as selective optimum doping method.

400 A difference in potential level between more than one types of  $\text{CuO}_2$  planes and a difference in energy level between the bands which these  $\text{CuO}_2$  planes possess can be used in this manner to permit the over-doped  $\text{CuO}_2$  plane and the optimum-doped to coexist in a unit lattice, and thus to have  $T_c$ ,  $J_c$  and  $H_{irr}$  of the superconductor raised considerably.

405 By the way,  $T_c$  varies with respect to the amount of doping, parabolically or along a parabolic curve opening downwards, whereon the optimum doping is established at the amount of doping at which  $T_c$  becomes maximum. In the case of Cu-oxide high temperature superconductors, this corresponds to the number of holes for one Cu (atom) that is 0.2 to 0.23. Further, over-doping indicates the amount of doping that is greater than that for optimum doping. Using the selective over-doping method according to the present invention gives rise to over-doping as a whole, but by the presence of an optimum-doped  
415 superconducting layer as mentioned above does not lower  $T_c$  despite over-doping.

Thus, in a Cu-oxide, selective reduction type, high temperature superconductor of the present invention, use is made of a change in the electronic and band structures formed  
420 by substitution of polyvalent reducible ions, e.g., Tl ions, for a portion of Cu ions in the charge supply layers to realize a mechanism that permits selective doping with positive holes.

This mechanism in a selective reduction type, high temperature superconductor of the present invention despite  
425 shortage of oxygen in the superconducting layers or against the inability to enough supply them with oxygen in the preparation step of the superconductor causes the substitute ions to pull electrons out of the superconducting layers and thus to supply them with positive holes. Accordingly, there  
430 results here no deterioration in properties as does if oxygen comes off, and then the preparation in an atmosphere of low oxygen partial pressure still permits yielding a high

temperature superconductor of high performance.

Further, given the superconducting layers formed in an  
435 over-doped state as suitably composed and structured, the use  
of this mechanism whereby selective doping by selective  
reduction permits the 5-coordination  $\text{CuO}_2$  plane to stay  
over-doped while rendering the 4-coordination  $\text{CuO}_2$  plane  
optimum-doped makes it possible to raise  $J_c$  while at the same  
440 time holding  $T_c$  high. In this case, the superconducting layers  
may, as suitably composed and structured, be formed also in  
an optimum-doped state.

While both optimum-doping and over-doping are described  
above as being controllable by decrease in the valence number  
445 of Tl ions by reduction in oxygen content, it is, of course,  
possible to control them by increase and decrease in oxygen  
content.

A selective reduction type, high temperature  
superconductor of the present invention as described above  
450 can be made first by preparing a high temperature  
superconductor by using high pressure synthesis, hot pressing,  
spattering, laser ablation or the like irreversible or  
non-equilibrium process of manufacture, and then by subjecting  
it to reduction heat-treatment.

455 The above-mentioned method of making according to the  
present invention is applicable to making selective reduction  
type, high temperature superconductors as can be described  
by the composition formula (a) mentioned below.

Composition Formula (a):

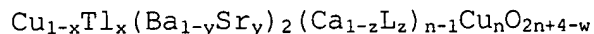
460  $\text{Cu}_{1-x}\text{M}_x(\text{Ba}_{1-y}, \text{Sr}_y)_2(\text{Ca}_{1-z}\text{L}_z)_{n-1}\text{Cu}_n\text{O}_{2n+4-w}$

where M represents ions of one or more polyvalent metallic  
elements selected from the class which consists of Tl, Bi,  
Pb, In, Ga, Sn, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, W, Re  
and Os; L represents one or more elements selected from the  
465 class which consists of Mg and alkaline metallic elements;  
 $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

The above-mentioned method of making according to the  
present invention is further applicable to making selective

reduction type, high temperature superconductors as can be  
470 described by the composition formula (b) mentioned below.

Composition Formula (b):



where L represents one or more elements selected from the class  
which consists of Mg and alkaline metallic elements;  $0 \leq x$   
475  $\leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ;  $0 \leq w \leq 4$ ; and  $1 \leq n \leq 16$ .

In order to prepare thin films of a Cu-oxide  
superconductor:

$\text{Cu}_{1-x}\text{M}_x(\text{Ba}_{1-y}, \text{Sr}_y)_2(\text{Ca}_{1-z}\text{L}_z)_{n-1}\text{Cu}_n\text{O}_{2n+4-w}$  having a layer structure  
according to the present invention, it is necessary that charge  
480 supply layers and superconducting layers be laid one on another  
alternately. Also required is that each layer be formed under  
accurate control of its composition and crystallinity and be  
of a large area.

This in turn requires, in addition to physical control  
485 such as for temperature and pressure, that additional element  
M exhibit its auto-forming capacity and that the crystal  
periodicity and atomic ordering in the  $\text{CuO}_2$  plane and in the  
direction perpendicular thereto be enhanced to an ideal level.  
An improvement in the in-plane ordering by the epitaxial effect  
490 an improvement in the crystallinity in the plane and in the  
direction perpendicular thereto by the chemical  
auto-formation effect of the additional element M result in  
a large improvement in the atomic ordering in the thin film  
crystal, which in turn contributes to a rise in  
495 superconductivity. An example of the additional element M is  
the utilization of  $M = \text{Tl}$  which possesses the structure  
stabilizing effect, the reaction accelerating effect, the  
charge supply effect and the  $T_c$  increasing effect together  
in combination. This additional element M has been found to  
500 exhibit the same or similar effects in forming high temperature  
superconductors other than those mentioned above. The method  
of making according to the present invention is designed to  
utilize the effects described above.

It should further be noted that a high temperature

505 superconducting material according to the present invention  
possesses a d-wave superconductivity by being a material that  
is large in Coulomb repulsion and of strong correlativity.  
As a result, it is considerably large in superconducting  
anisotropy in the  $\text{CuO}_2$  plane. This anisotropy can be made  
510 smaller by the selective reduction of the present invention.  
To wit, as shown in Fig. 8, performing the selective reduction  
brings electrons in the  $\text{CuO}_2$  plane into a  $[d + is]$  state where  
an s-wave property is introduced that is characteristic of  
a superconducting material of weak correlativity. This leads  
515 to realization of a high performance superconducting material  
that is small in anisotropy.

It is thus seen that the method of making according to  
the present invention achieves the preceding effect as well.

Mention is next made of a first, preferred form of  
520 embodiment of the invention represented by an example having  
a composition:  $(\text{Cu}_{1-x}\text{Tl}_x)\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  where  $0 \leq x \leq 1.0$  and  $0 \leq y \leq 1$ ,  
and having a structure with a unit lattice illustrated  
in Fig. 2A. The structure of specimen for this first form of  
embodiment of the invention as indicated in Fig. 2A is  
525 referred to here as Cu-1223.

An explanation is first given in respect of a method  
of making this first form of embodiment of the invention.

Raw materials to make up a selective reduction type,  
high temperature superconductor as the first form of  
530 embodiment of the invention are:  $\text{CuO}$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_2$ ,  $\text{BaO}_2$  and  
 $\text{CaO}_2$  with an oxidizing agent such as of  $\text{AgO}$  or  $\text{CaO}_2$  and a reducing  
agent such as of  $\text{Cu}_2\text{O}$ .

First, a precursor of  $\text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_7$  has  $\text{CuO}$  and  $\text{Tl}_2\text{O}_3$  mixed  
therewith in a proper amount, and a specimen having a  
535 composition:  $(\text{Cu}_{1-x}\text{Tl}_x)\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  ( $x = 0.5$ ) is prepared by  
synthesis in a cubic angle high pressure generating apparatus  
under conditions of  $85^\circ\text{C}$ , 5 Gpa and 2 hours.

Next, this specimen is annealed in a reducing atmosphere,  
e.g., of nitrogen gas, of a temperature range from  $400^\circ\text{C}$  to  
540  $700^\circ\text{C}$ , preferably at  $540^\circ\text{C}$  for a period of 12 hours. This

selective reduction treatment gives rise to a selective reduction type, high temperature superconductor of this form of embodiment of the invention.

What is to be mentioned further is that the  
545 above-mentioned method of making according to the present invention is also applicable to making selective reduction type, high temperature superconductors as can be described by the composition formula (c) mentioned below.

Composition Formula (c):

550 
$$\text{Cu}_{1-x}\text{M}_x(\text{Ba}_{1-y}, \text{Sr}_y)_2(\text{Ca}_{1-z}\text{L}_z)_{n-1}\text{Cu}_n\text{O}_{2n+4-w}$$

where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

An explanation is next given in respect of properties  
555 of the first form of embodiment of the invention.

Fig. 3 is a diagram that indicates the temperature dependency of the electrical resistivity for various temperatures at which annealing is effected (for specimens) in the first form of embodiment.

560 As shown in Fig. 3,  $T_c$  rises from 97 K to 131 K as the annealing temperature is raised. The curves' gradient varies somewhat in the vicinity of  $T_c$  for the annealing temperatures from 350°C to 450°C, apparently due to ununiformity of the specimen. A normal conduction electrical resistivity rises  
565 for the annealing temperature that is raised from 200°C to 400°C, and then falls for the annealing temperature of 400°C to 550°C, followed by a rise at the annealing temperature of 600°C.

Fig. 4 is a diagram showing thermo-analysis data in  
570 the first form of embodiment of the invention.

From the results of the thermo-gravimetric analysis (TG), it is shown that the weight decreases as the annealing temperature is raised and especially that it falls sharply in the vicinity of 400°C and in excess of 700°C. From the results of the  
575 differential thermo-analysis (DTA), it is also seen that the losses in weight near 400°C and more than 700°C are each due



to emission of oxygen and Tl.

Fig. 5 is a diagram showing that the hole density changes with the temperature in the first form of embodiment of the invention.

As shown in Fig. 5, the carriers for Cu found from measurement of Hall coefficient has a density of 0.5 at the temperature of 300 K for a specimen as it is formed by high pressure synthesis, which leaves the specimen over-doped. However, annealing changes the carrier density. Thus, while annealing at 400°C reduces the carrier density to 0.12 and brings the specimen into an under-doped state, annealing at 540°C gives rise to a carrier density of 0.2 and brings the specimen almost into an optimum-doped state. Fig. 6 is a diagram showing relationships between  $T_c$  of a specimen in the first form of embodiment of the invention annealed, its normally conducting electrical resistivity, carrier density and weight's rate of change and the annealing temperature.

Referring to Fig. 6, annealing a specimen in an over-doped state causes oxygen to come out of it, resulting in a decreases in its carrier concentration and hence a rise in  $T_c$ . At the annealing temperature of 400°C, oxygen coming off radically brings the specimen into an under-doped state while maintaining  $T_c$  high.

A rise further in the annealing temperature further decreases the oxygen concentration, but is followed by a change in electronic state which increases the carrier concentration so it nears its optimum doping amount. And at the annealing temperature of 540°C,  $T_c$  becomes its maximum. And ye, at any temperature of 700°C or more, oxygen further coming off causes the specimen to deteriorate.

The phenomenon that a change in electronic state increases the carrier concentration has been mentioned before in connection with figs. 7 and 8, and can be explained as follows: To wit, Tl ions present in charge supply layers are trivalent (+3) and Tl6s level lies above the Fermi level ( $E_s$ ) if the oxygen concentration is high. As the oxygen

concentration lowers, Tl ions are reduced to become monovalent (+1) and the Tl6s level becomes lower than the Fermi level.

615 This causes Tl ions to pull electrons out of the 5-coordination CuO<sub>2</sub> surface that is a superconducting layer and conversely to supply the superconducting, 5-coordination CuO<sub>2</sub> surface with holes.

In this manner, selective reduction of Tl ions can  
620 supply holes, thereby increasing the carrier concentration.

It should be noted at this point that from measurement of changes in the upper critical magnetic field, a selective reduction type high temperature superconductor is found to have coherence length of 3 Å or more. Also, from measurement  
625 of the ratio of the upper critical magnetic field in the c-axis to those in the a- and b-axes, its superconducting anisotropy is found to be 10 or less.

Mention is next made of a second, preferred form of embodiment of the invention.

630 This second form of embodiment is a thin film of a selective reduction type high temperature superconductor having a composition: (Cu<sub>1-x</sub>Tl<sub>x</sub>) (Ba, Sr)<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> with the structure, like that of the afore-mentioned first form, as shown Fig. 2A.

635 Continued, an explanation is given in respect of a method of making for the second form of embodiment.

First, a precursor component Cu-Ba-Ca-O has Tl<sub>2</sub>O<sub>3</sub> uniformly mixed therewith in an amount of 0.25 to 0.5 mol to prepare:

640 Cu<sub>1-x</sub>Tl<sub>x</sub>Ba<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>y</sub> where x = 0.25 to 0.5, and by pressing to form thallium mixed pellets each of a diameter of 10 mm and a weight of about 450 mg.

Next, such a thallium mixed pellets is pre-heated for 1 hour to prepare a pellet for thallium adjustment.

645 Next, a SrTiO<sub>3</sub> substrate has an amorphous film of (Cu<sub>1-x</sub>Tl<sub>x</sub>) (Ba, Sr)<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> built up thereon by RF magnetron sputtering using, for example, a sintered TlBaSrCa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> body as a target.

Subsequently, the  $\text{SrTiO}_3$  substrate having the  
650 amorphous film built up thereon, the thallium mixed pellet  
and the pellet for thallium adjustment are encapsulated in  
a capsule made of Au, Ag or Pt and then are heat-treated at  
a temperature of  $860^\circ\text{C}$  to  $890^\circ\text{C}$  for a period of 30 to 90 minutes  
to cause an epitaxy film of  $(\text{Cu}_{1-x}\text{Tl}_x)(\text{Ba}, \text{Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_y$  to  
655 epitaxially grow from the amorphous film. This process will  
be referred to below as "amorphous phase epitaxy (APE)  
process".

The superconductor film of  $(\text{Cu}_{1-x}\text{Tl}_x)(\text{Ba}, \text{Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_y$   
obtained by the APE process is annealed in a low oxygen gaseous  
660 atmosphere of 1 atm or less at a temperature of  $500^\circ\text{C}$  for a  
period of 30 minutes to prepare a selective reduction type,  
high temperature superconductor of the composition with  $x =$   
0.4 to 0.8 as the second form of embodiment of the invention.

It should be noted here that the method of making  
665 described above for the second form of embodiment is applicable  
to a (Cu, M) family, high temperature superconductor as well  
with the composition formula (c) mentioned in connection with  
the first form of embodiment of the invention. Here again  
as there, selective reduction can yield a positive hole dopable,  
670 high temperature superconductor.

The second form of embodiment of the invention is  
advantageous in that it gives rise to  $J_c$  that is so high as  
 $J_c = 1 \times 10^6$  to  $2 \times 10^7 \text{ A/cm}^2$  (77K, 0T).

Fig. 9 is a diagram showing an X-ray analysis pattern  
675 of a specimen in the second form of the invention.

As shown in Fig. 9, a strong (001) peak is found,  
indicating that a c-axis orientation is the case. The c-axis  
here has a lattice constant of  $15.89\text{\AA}$  that lies between  $14.79$   
 $\text{\AA}$  of a Cu-oxide high temperature superconductor and  $15.93$   
680  $\text{\AA}$  of Tl-oxide high temperature superconductor.

Also, from observation of X-ray culminating (peak,  
extreme) points it has been confirmed that an in-plane  
orientation is the case ( $\Delta\phi = 0.5$  to  $1.5$  degree).

It has further been shown that the composition

685  $(\text{Cu}_{1-x}\text{Tl}_x)(\text{Ba}, \text{Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_y$  if annealed at a temperature of 870 to 900°C for a period of 30 to 90 minutes has  $T_c = 96$  to 115 K and  $J_c = 1 \times 10^6$  to  $2 \times 10^7$  A/cm<sup>2</sup> (77K, 0T).

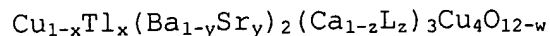
Mention is next made of a third, preferred form of the present invention. The selective reduction type high  
690 temperature superconductor in the third form of embodiment is a superconductor film of  $n = 4$ , the composition  $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$  having a structure as shown in Fig. 2B. This structure as indicated in the Figure is referred to herein as Cu-1234.

695 An explanation is given in respect of a method of making a superconductor in the third form of embodiment of the invention.

A  $\text{SrTiO}_3$  substrate has an amorphous film of  $(\text{Cu}_{1-x}\text{Tl}_x)\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$  built up thereon by RF magnetron  
700 sputtering using a sintered body composed of  $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$  as a target.

The amorphous film, together with pellets as mentioned in connection with the second form of embodiment, in a capsule made of Au, Ag or Pt and then is heat-treated at a temperature  
705 of 880°C to 920°C for a period of 1 hour. Further, the heat-treated amorphous film after having an electrode film of Au deposited thereon is annealed in a low oxygen gaseous atmosphere of 1 atm or less at a temperature of 450 to 500°C for a period of 30 minutes to prepare a selective reduction  
710 type high temperature superconductor as the third form of embodiment of the invention.

The preceding method used to make a superconductor in the third form of embodiment is applicable to making a selective reduction type high temperature superconductor that  
715 can be indicated by composition formula (d):



where L represents one or more elements selected from the class which consists of Mg and alkaline metallic elements;  $0 \leq x \leq 1.0$ ;  $0 \leq y \leq 1$ ;  $0 \leq z \leq 1$ ; and  $0 \leq w \leq 4$ .

720 An explanation is next given in respect of properties

of a selective reduction type high temperature superconductor according to the third form of embodiment of the present invention.

725 X-ray analysis of the thin film shows that it has a lattice constant of 18.9 to 18.5 Å that lies between 17.99 Å of Cu-1234 and 19.11 Å of Tl-1234.

The X-ray peak pattern has a half-width  $\Delta = 0.5$  to 1.5, indicating a good orientation in the a-b plane.

730 Further, from composition analysis by an energy distribution type composition analyzer (EDX), it has been found that  $x = 0.4$  to 0.8 and from measurement of electrical resistivity  $T_c$  has been found to be 100 to 115 K.  $J_c$  has been found to lie between 1 and  $2 \times 10^6$  A/cm<sup>2</sup>. Improving the preparation process may further rise both  $T_c$  and  $J_c$ .

735 While a method of making a selective reduction type, high temperature superconductor according to the present invention permits changing  $n$  by its preparation composition or the preparation composition of the target material, it should be noted that the  $n$  can be changed by changing the  
740 reaction temperature and the treatment time period as well. A selective reduction type high temperature superconductor of optimum properties has currently been found to be obtainable with  $n$  of 4 to 6 and a thickness of unit lattice  $(\text{CaCuO}_2)_n$  of 10 to 16 Å.

745 Although the present invention has hereinbefore been set forth with respect to certain illustrative forms of embodiments thereof, it will readily be appreciated to be obvious to a person skilled in the art that many alternations thereof, omissions therefrom and additions thereto can be made  
750 without departing from the essences of scope of the present invention. Accordingly, it should be understood that the invention is not intended to be limited to the specific forms of embodiment thereof set forth below, but to include all possible forms of embodiment thereof that can be made within  
755 the scope with respect to the features specifically set forth in the appended claims and encompasses all the equivalents

thereof.

#### Industrial Applicability

As has been set forth in the foregoing description,  
760 a selective reduction type high temperature superconductor  
and a method of making the same according to the present  
invention are extremely useful in the superconducting  
electronics industry that involves large scale  
superconducting power transmission, superconducting power  
765 storage or reserve, superconducting electronic components  
such as a high performance Josephson device, a high frequency  
device or the like.